Tetrahedron Letters No. 23, pp 1951 - 1954, 1977. Pergamon Press. Printed in Great Britain.

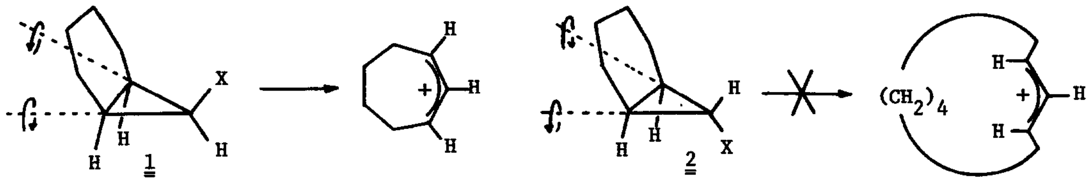
IONIC PERICYCLIC REACTIONS. A SEARCH FOR THE RETRO-CYCLOADDITION OF CYCLOPROPENIUM ION WITH BENZENE

Ronald M. Magid* and Gary W. Whitehead

Department of Chemistry, The University of Tennessee
Knoxville, Tennessee 37916

(Received in USA 5 January 1977; received in UK for publication 29 April 1977)

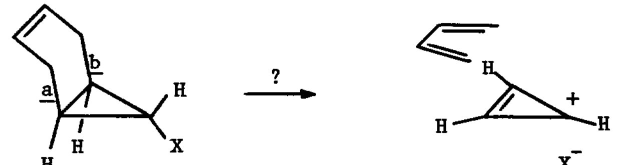
The facile ionization of *endo*-substituted bicyclo[4.1.0]hexanes 1 and the reluctance of the epimeric *exo* compounds 2 to behave similarly[1,2] served as one of the early triumphs of the predictive powers of the orbital symmetry rules.[3,4] In addition to the kinetic data, product studies revealed a sharp difference between 1 and 2 (and molecules related to them): whereas monocyclic allylic products were obtained from 1, 2 often yielded unrearranged materials in which the integrity and stereochemistry of the three-membered ring were retained.[1-4]



1

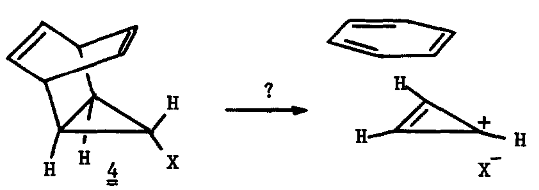
2

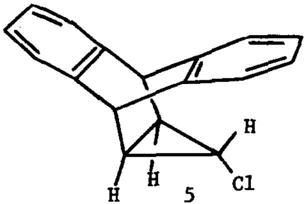
We became interested in learning if introduction of a double bond into 2 would provide a new symmetry-allowed ionization pathway. That is, as heterolysis of the C-X bond in 3 occurs, simultaneous cleavage of bonds *a* and *b* would constitute the *retro* Diels-Alder reaction of butadiene with cyclopropenium ion. Although no concerted cycloaddition of a cyclopropenium ion has been documented, the related aromatic compound cyclopropenone and its derivatives do give Diels-Alder and 1,3-dipolar additions with the appropriate reaction partners;[5] tropylium ion also undergoes what appear to be concerted, symmetry-allowed[6] cycloadditions with dienes and trienes.[7] Furthermore, a Diels-Alder reaction of cyclopropenium ions with dienes has been proposed to account for the reactivity of halocyclopropenes.[8] To further entice a molecule to avail itself of this *retro* ionic cycloaddition, we decided to introduce an etheno bridge into 3; cleavage of 4 would, then, produce two aromatic compounds.



3

Numerous bicyclic and tricyclic materials related to 3 have been prepared,[9] but none undergoes the postulated conversion. The only reported compound of the 4-type is dibenzo derivative 5; treatment with AgOAc in refluxing acetic acid for prolonged periods gave *no* AgCl and

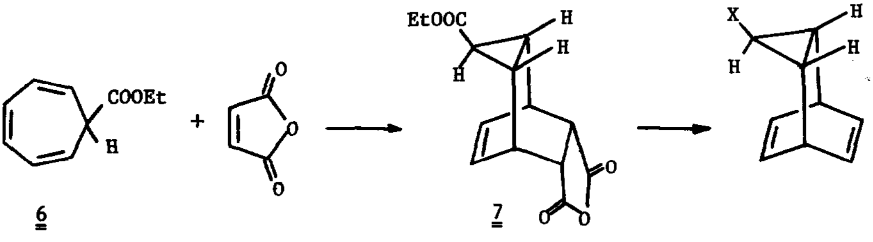




5

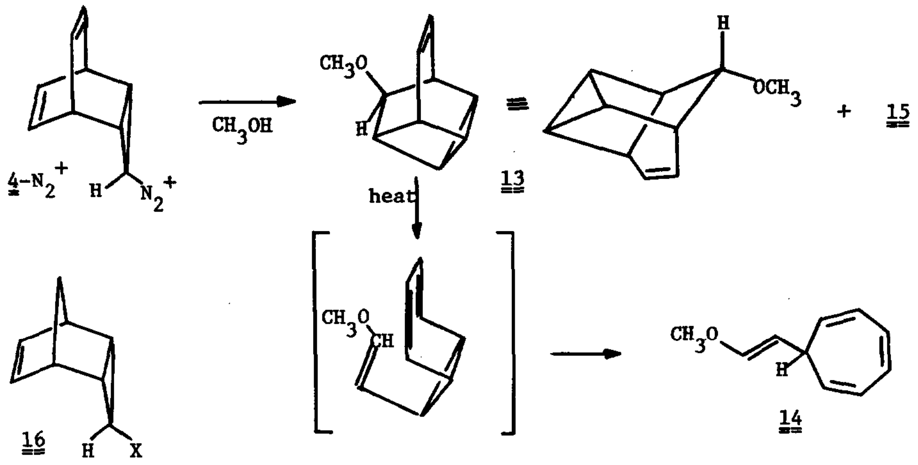
resulted in quantitative recovery of starting material.[4b,d] This intransigence toward ionization is one of the more striking confirmations of the orbital symmetry rules, but the failure of 5 to cleave might simply be a reflection of the rather meager increase in resonance energy for the formation of anthracene along with cyclopropenium ion and chloride. We now report the generation of 4-N_2^+ and the structures of its solvolysis products in methanol.

Reaction of 7-carbethoxycycloheptatriene 6[10] (75% of a mixture consisting of 6 and its H-shifted isomers) with maleic anhydride for two days at room temperature[11,12] gave a 90% isolated yield of the known Diels-Alder adduct 7; evidence for the exo orientation of the ester group is the small coupling constant (t, J = 3Hz) of the adjacent carbinyl proton.[13] Oxidative decarboxylation with bis(triphenylphosphine)dicarbonylnickel[14] in diglyme at 270° afforded tricyclic ester 8[13] in 24% yield; unreacted anhydride 7 was found in the residue from distillation. Saponification of 8 with NaOH in aqueous ethanol produced acid 9[13] (70% isolated yield) which was treated with triethylamine and ethyl chloroformate;[15] reaction of the unisolated mixed anhydride with NaN_3 followed by thermolysis[15] of the resulting acid azide at 100° gave isocyanate 10[13] in 87% yield. Conversion into urea 11[13] (satisfactory C,H,N analysis) with anhydrous NH_3 (70% yield) followed by nitrosation[15b] with $NaNO_2$ in acetic acid/acetic anhydride gave 47% of nitrosourea 12.[13]

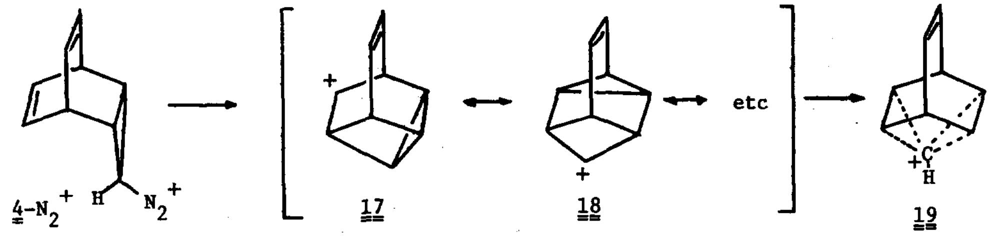


8 X = -COOEt
9 X = -COOH
10 X = -N=C=O
11 X = -NH-CO-NH_2
12 X = -N(NO)-CO-NH_2

Treatment of nitrosourea 12 with Na_2CO_3 in methanol[9d,e,16] generated the desired diazonium ion 4-N_2^+. A careful search for benzene in the reaction mixture failed to reveal the existence of the postulated retro ionic cycloaddition. Instead, a low yield of a difficult-to-separate mixture of three ethers in the ratio 90:5:5 was obtained. The major component, isolated by preparative glpc, was identified as tetracyclic ether 13 through analysis of its NMR and ir spectra[21] and its conversion by diimide reduction into the known dihydro derivative.[17] One of the minor components is formed in the injection port during glpc analysis[18] and was identified[22] as enol ether 14 by comparison with a sample prepared from the known[19] 7-cycloheptatrienylacetaldehyde; the other component 15, a primary product, might be the ether from apical attack on 19 (analogous to the related material[9c-f] produced from 16, X = OTf or N_2^+), but the minute amounts available prevented any complete characterization.



Thus, loss of N_2 from 4-N_2^+ occurs with simultaneous (or subsequent) participation of the double bond giving ion 17, in equilibrium (or resonance) with 18; as such, its chemistry is analogous to that of triflate or diazonium ion 16.[9c-f] Our solvolysis data do not establish the structure of the carbonium ion intermediate, but NMR studies of the ion in SbF_5/FSO_2Cl[17] are consistent with its having the highly delocalized pyramidal structure 19.[20]



Acknowledgments: Acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research. G.W.W. thanks the National Defense Education Act for a Fellowship.

REFERENCES AND NOTES

1. Reviews: (a) U. Schöllkopf, Angew. Chem., Int. Ed. Engl., 7, 588 (1968); (b) C. H. DePuy, Chem. Rev., 74, 605 (1974).

2. See the following recent reports and references cited therein: (a) W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, J. Am. Chem. Soc., 94, 133 (1972); (b) L. Radom, P. C. Harihara J. A. Pople, and P. v. R. Schleyer, ibid., 95, 6531 (1973); (c) P. Warner, S-L. Lu, E. Myers, P. W. Deltaven, and R. A. Jacobson, Tetrahedron Lett., 4449 (1975); (d) C. B. Reese and A. Shaw, J. Chem. Soc., Perkin Trans. 1, 2422 (1975); (e) X. Creary, J. Org. Chem., 41, 3734, 3740 (1976); (f) X. Creary, J. Am. Chem. Soc., 98, 6608 (1976).

3. R. B. Woodward and R. Hoffmann, Angew. Chem., Int. Ed. Engl., 8, 781 (1969).

4. (a) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, J. Am. Chem. Soc., 87, 4006 (1965); (b) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, ibid., 87, 4007 (1965); (c) C. H. DePuy, L. G. Schnack, and J. W. Hausser, ibid., 88, 3343 (1966); (d) S. J. Cristol, R. M. Sequeira, and G. O. Mayo, ibid., 90, 5564 (1968); (e) C. H. DePuy, Acc. Chem. Res., 1, 33 (1968); (f) U. Schöllkopf, K. Fellenberger, M. Patsch, P. v. R. Schleyer T. Su, and G. W. van Dine, Tetrahedron Lett., 3639 (1967).

5. (a) R. Breslow and M. Oda, *J. Am. Chem. Soc.*, **94**, 4787 (1972); (b) M. Oda, R. Breslow, and J. Pecoraro, *Tetrahedron Lett.*, 4419 (1972); (c) T. Sasaki, K. Kanematsu, Y. Yukimoto, and E. Kato, *Synth. Commun.*, **3**, 249 (1973); (d) A. Hassner and A. Kascheres, *J. Org. Chem.*, **37**, 2328 (1972); (e) K. T. Potts and J. Baum, *J. Chem. Soc., Chem. Commun.*, 833 (1973); (f) H. Matsukubo and H. Kato, *ibid.*, 412 (1974); (g) M. L. Deem, *Synthesis*, 675 (1972).

6. For an orbital symmetry analysis of the cycloaddition of aromatic compounds, see: (a) D. Bryce-Smith, *J. Chem. Soc., Chem. Commun.*, 806 (1969); (b) D. Bryce-Smith and A. Gilbert, *Tetrahedron*, **32**, 1309 (1976).

7. (a) S. Ito and I. Itoh, *Tetrahedron Lett.*, 2969 (1971); (b) S. Ito, A. Mori, I. Saito, K. Sakan, H. Ishiyama, and K. Sasaki, *ibid.*, 2737 (1973); (c) S. Ito, I. Itoh, I. Saito, and A. Mori, *ibid.*, 3887 (1974).

8. R. M. Magid and S. E. Wilson, *J. Org. Chem.*, **36**, 1775 (1971).

9. (a) P. M. Warner, R. C. LaRose, R. F. Palmer, C-M. Lee, D. O. Ross, and J. C. Clardy, *J. Am. Chem. Soc.*, **97**, 5507 (1975); (b) D. B. Ledlie, T. Swan, J. Pile, and L. Bowers, *J. Org. Chem.*, **41**, 419 (1976); (c) A. V. Kemp-Jones, N. Nakamura, and S. Masamune, *J. Chem. Soc., Chem. Commun.*, 109 (1974); (d) W. Kirmse and T. Olbricht, *Chem. Ber.*, **108**, 2606, 2616 (1975); (e) W. Kirmse, *Angew. Chem., Int. Ed. Engl.*, **15**, 251 (1976); (f) X. Creary, *J. Org. Chem.*, **40**, 3326 (1975).

10. W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960).

11. As reported[12] for a similar mixture of the methyl esters, only the 7-isomer reacts under these conditions.

12. A. Ritter, P. Bayer, J. Leitich, and G. Schomburg, *Justus Liebigs Ann. Chem.*, 835 (1974).

13. Tricyclic and tetracyclic compounds **7**-**12** displayed NMR spectra entirely consistent with the structures shown and analogous to spectra of related materials in the literature; for each, the carbinyl H adjacent to the functional group had the small coupling constant (*J* = 2-3 Hz) typical of *trans* coupling in a three-membered ring.

14. W. G. Dauben, G. T. Rivers, R. J. Twieg, and W. T. Zimmerman, *J. Org. Chem.*, **41**, 887 (1976).

15. (a) J. Weinstock, *ibid.*, **26**, 3511 (1961); (b) W. M. Jones, M. H. Grasley, and W. S. Brey, *J. Am. Chem. Soc.*, **85**, 2754 (1963).

16. S. M. Hecht and J. W. Kozarich, *Tetrahedron Lett.*, 5147 (1972).

17. See the accompanying communication by R. M. Coates and E. R. Fretz. We are grateful to Professor Coates for supplying us with spectra and an authentic sample of the dihydro ether.

18. For related intramolecular Diels-Alder reactions, see the following recent reviews and articles: (a) R. G. Carlson, *Ann. Rept. Med. Chem.*, **9**, 270 (1974); (b) G. Mehta, *J. Chem. Educ.*, **53**, 551 (1976); (c) W. Oppolzer and R. L. Snowden, *Tetrahedron Lett.*, 4187 (1976).

19. M. E. Volpin, I. S. Akhrem, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1530 (1957).

20. Two recent reviews on such species have appeared: (a) H. Hogeveen and P. W. Kwant, *Acc. Chem. Res.*, **8**, 413 (1975); (b) S. Masamune, *Pure Appl. Chem.*, **44**, 861 (1975).

21. *exo*-6-Methoxytetracyclo[3.2.2.$0^{2,4}$.$0^{3,7}$]non-8-ene (**13**): ^{1}H-NMR (CCl_4) δ 1.3-1.9 (m, 4, H_2, H_4, H_3, H_7); 2.2 (m, 1, H_1); 2.9-3.3 (m, 4, H_5 and $-OCH_3$ (singlet at δ 3.0)); 3.5 (m, 1, H_6); 6.1 (t, 2, *J* = 4 Hz, H_8, H_9).

22. 2-(7'-Cycloheptatrienyl)-1-methoxyethene (**14**): ^{1}H-NMR (CCl_4) δ 2.1 (m, 1, $H_{7'}$); 3.45 (s, 3, $-OCH_3$); 4.0 and 4.6 (m, 1, H_2, *Z* and *E* isomers); 5.1 (m, 2, $H_{1'}$, $H_{6'}$); 6.0 (m, 3, H_1, $H_{2'}$, $H_{5'}$); 6.5 (m, 2, $H_{3'}$, $H_{4'}$).